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ORGANIC SYNTHESIS  
AND INDUSTRIAL ORGANIC CHEMISTRY

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## Liquid-Phase Oxidation of Bromovinyl Compounds with Molecular Oxygen

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Received June 16, 2005; in final form, March 2006

**Abstract**—Liquid-phase oxidation of bromovinyl compounds with the aim to obtain the corresponding  $\alpha$ -bromo acids was studied.

**DOI:** 10.1134/S1070427206110218

$\alpha$ -Bromo acids and their derivatives are of interest as intermediates in the synthesis of drugs, insecticides, fungicides, plasticizers, and stabilizers of polymers and  $\alpha$ -amino acids against thermal oxidative degradation [1–5].

Data on liquid-phase oxidation of bromovinyl compounds are scarce [6–10]. Demole [6, 7] reported only qualitative data on the liquid-phase oxidation of bromovinyl compounds; Pericas and Serratos [8] studied the stereochemistry of liquid-phase oxidation with molecular oxygen of certain 1-bromo-1,2-diisopropoxyethenes and showed that these compounds are very sensitive to oxygen. In particular, bubbling of oxygen through a dilute solution of 1-bromo-1,2-diisopropoxyethene in pentane results in an exothermic reaction; the oxidation is complete in 1.5 h. The reaction product, isopropyl isopropoxybromoacetate, was isolated in 87% yield by distillation after removing the solvent. Oxidation of 1,2-dibromo-3,3-diphenylmethylene-1,2-cyclobutene with molecular oxygen in benzene [9] occurs at the endocyclic double bond, with the migration of a bromine atom. The kinetics of autooxidation of tribromoethene in chlorobenzene at 303 and 313 K was studied by monitoring the oxygen uptake rate [10]. The reaction was shown to occur by the branched radical-chain mechanism; its major final stable products were bromooxirane and dibromoacetic anhydride. A probable mechanism of the autooxidation of tribromoethene was suggested.

Previously we studied the oxidation with molecular oxygen of a series of 1,1-dichloro- and 1,1-dibromochlorovinyl compounds and found that the reactions were highly selective and gave  $\alpha$ -haloacyl chlorides in

high yields [11–22]. It seemed interesting to study oxidation with molecular oxygen of bromovinyl compounds, with the aim to compare the results and discuss the general mechanism of oxidation of halovinyl compounds.

Proceeding with studies on oxidation of halovinyl compounds, we examined the oxidation of 1,2-dibromoethene **I** (1 : 4 *cis/trans* isomer mixture), tribromoethene **II**, tetrabromoethene **III**,  $\beta,\beta$ -dibromostyrene **IV**, and  $\alpha,\beta,\beta$ -tribromostyrene **V**.

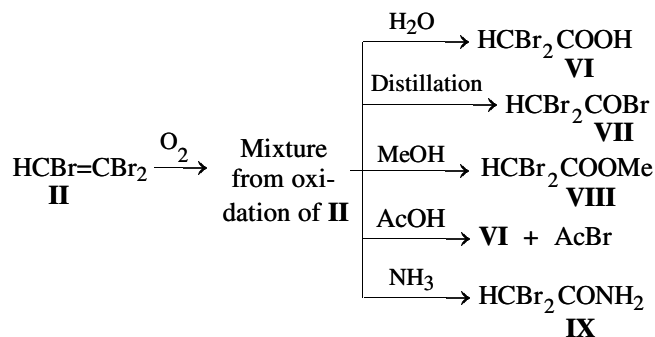
Experiments were performed on a laboratory installation in the temperature range 20–100°C at an oxygen feeding rate of 2–5 l h<sup>–1</sup>.

The experiments revealed formation of bromooxiranes in the early oxidation steps; their content reaches 45–60% (determined iodometrically) at 70–80% conversion. Upon distillation, they transform into  $\alpha$ -bromoacyl bromides. The only product of oxidation of **I** is dibromoacetic acid **VI**. A more detailed study of the oxidation of **II** with oxygen showed that pentabromoethane was also formed (15–20%) along with dibromoacetyl bromide **VII**. The amount of pentabromoethane depended on the oxidation conditions. For example, its formation was suppressed by increasing reaction temperature and oxygen feeding rate. This result can be attributed to partial removal of the released free bromine from the reaction mixture. However, the formation of free bromine does not appreciably affect the yield of **VII** (80–90% at 100% conversion).

Free bromine can be formed in the system by the reaction of HBr with peroxides accumulating in the

mixture, or by photochemical decomposition of **II** and its oxidation products.

Whereas direct distillation of the reaction mixture from the oxidation of **II** yielded acid bromide **VII**, treatment of the same mixture with water, acetic acid, alcohols, and ammonia yielded the corresponding products **VI**, **VIII**, and **IX**:



Oxidation of tetrabromoethene **III** gave tribromoacetyl bromide in high yield.

Under the similar conditions, the oxidation of **IV** and **V** gave bromo- and dibromophenylacetyl bromides, respectively, in 70–80% yields; as compared to **II**, these compounds are oxidized very slowly, i.e., the oxidation rate is strongly affected by the aromatic substituent.

The structure and purity of the compounds were checked by comparison of their physicochemical constants with the published data, and also by GLC.

The most interesting feature of liquid-phase oxidation of bromovinyl compounds with oxygen is high selectivity of the reaction at temperatures below 70°C, with the formation of  $\alpha$ -bromoacetyl bromides. With an increase in the temperature, the oxidation rate increases insignificantly, but the selectivity is lost, and other products, including polymers, are formed along with acyl bromides.

## EXPERIMENTAL

The starting bromovinyl compounds **IV** and **V** were prepared according to [23], and **I–III**, by modified procedures from [24]; their physicochemical constants agree with the published data.

The starting compounds and final products were analyzed with a Tsvet-800 chromatograph equipped with a thermal conductivity detector; 3000  $\times$  3-mm glass column, stationary phase E-301 + polyethylene glycol adipate (5% each) on Inerton Super (0.16–0.20 mm), column temperature 50–250°C, carrier gas He (40–60 ml min<sup>-1</sup>).

**cis,trans-1,2-Dibromoethene I.** A 250-ml flask equipped with a reflux condenser and a thermometer was charged with 172.9 g of 1,1,2,2-tetrabromoethane and 36.5 g of dimethylformamide, after which 14 g of iron powder was gradually added. The reaction was exothermic, and the reaction mixture, if necessary, was cooled with water. After the reaction completion, the mixture was distilled to give 86.7 g (93%) of a mixture of *cis*- and *trans*-dibromoethenes **I** in a 1 : 4 ratio (GLC data); bp 102–105°C (680 mm Hg),  $D_4^{20} = 2.2754$ ,  $n_D^{20} = 1.5458$  [25].

**Tribromoethene II.** A mixture of 16 g of NaOH, 20 ml of water, 2 g of a 50% aqueous solution of Katamin AB, and 148.3 g of 1,1,2,2-tetrabromoethane was stirred for 2 h at 25–30°C. The organic layer was separated and dried over CaCl<sub>2</sub>; distillation gave 95.3 g (90%) of tribromoethene **II**, bp 53–55°C (10 mm Hg),  $D_4^{20} = 2.7080$ ,  $n_D^{20} = 1.6040$  [26]. The product purity (GLC data) was 99.2%.

**Tetrabromoethene III** was prepared similarly to **II** from 169.8 g of pentabromoethane; yield 126.8 g (92%), bp 100–102°C (16 mm Hg), crystallizes during distillation, mp 55–56°C (from ethanol) [27]. The product purity (GLC data) was 98.6%.

**$\alpha$ -Bromoacetyl bromides.** A glass reactor 35 mm in diameter and 1 m high, equipped with a porous bubbler, an efficient reflux condenser, and a sampler was charged with dibromovinyl compounds freshly distilled from P<sub>2</sub>O<sub>5</sub> (0.01 mol %); the vessel was placed in a thermostat. The temperature of 70°C was maintained, and technical-grade oxygen was fed at a rate of 2–4 l h<sup>-1</sup>. Before entering the vessel, oxygen was purified by passing through two U-shaped tubes, one of which was packed with CaCl<sub>2</sub>, and the other, with KOH, through a Tishchenko bottle with P<sub>2</sub>O<sub>5</sub>, and through a trap. All the parts of the system were connected with rubber tubes. The reaction completion was judged from the disappearance of the peak of the starting bromovinyl compound in the GLC pattern.

**Oxidation of 1,2-dibromoethene I.** A mixture of *cis*- and *trans*-dibromoethenes **I** (18.6 g) was oxidized with oxygen (3 l h<sup>-1</sup>) at 30°C for 20 h. Vacuum distillation of 10 g of the oxidation products gave 7.4 g (74%) of dibromoacetic acid, bp 68–69°C (2 mm Hg). This compound gradually crystallizes on storage at 20°C; mp 48°C [28].

**Oxidation of tribromoethene II.** The reactor was charged with 3.5 kg of tribromoethene **II** and heated to 70°C; at this temperature, oxygen was fed (15–20 l h<sup>-1</sup>) for 250 h. We obtained 3.69 kg of oxidation products. Vacuum distillation of their 300-g portion

gave 205.9 g (80%) of dibromoacetic anhydride **VII**, bp 77–80°C (10 mm Hg),  $D_4^{20} = 1.8236$ ,  $n_D^{20} = 1.5480$  [29].

**Dibromoacetic acid VI.** Water (1.5 l) was slowly added with cooling and stirring to 2100 g of the oxidation products of **II**. The mixture was allowed to stand at 20°C for 12 h, after which the insoluble fraction (287.5 g, tetrabromoethene : pentabromoethane = 95.8 : 4.2) was separated from the aqueous layer. Acetic acid (200 ml) was added to the aqueous layer, and the mixture was distilled under reduced pressure (water-jet-pump vacuum); the residue was distilled in a vacuum. Acid **VI** was obtained; yield 1219.2 g (88% based on converted **II**), bp 128–130°C (16 mm Hg), crystallizes in the course of distillation, mp 46°C [28].

**Methyl dibromoacetate VIII.** A three-necked flask equipped with a dropping funnel, a thermometer, and a reflux condenser was charged with 150 g of oxidation products of **II**, and 30 ml of absolute methanol was slowly added with cooling and stirring from a dropping funnel. After completion of the exothermic reaction and release of HBr, excess methanol was removed, and the residue was distilled. Ester **VIII** was obtained; yield 108.2 g (87%), bp 178–180°C (680 mm Hg),  $D_4^{20} = 1.8711$ ,  $n_D^{20} = 1.9137$  [29].

**Oxidation of tetrabromoethene III.** The reactor was charged with 68.9 g of **III** and heated to 90°C; at this temperature, oxygen was fed (2.5–3 l h<sup>-1</sup>) for 90 h. We obtained 71.8 g of oxidation products. Vacuum distillation of their 16.8-g portion gave 13.2 g (79%) of tribromoacetic anhydride, bp 90–92°C (12 mm Hg),  $D_4^{20} = 2.6510$ ,  $n_D^{20} = 1.8518$  [30].

**Tribromoacetic acid X.** Water (15 ml) was slowly added with cooling to 20 g of oxidation products of **III**; the mixture was allowed to stand at 20°C for 12 h, and excess water was removed in a water-jet-pump vacuum. The residue was recrystallized from ethanol; yield of **X** 13.8 g (84%), mp 129–131°C [30].

**Ethyl tribromoacetate XI.** Absolute ethanol (15 ml) was slowly added from a dropping funnel with cooling (water–ice) to 20 g of oxidation products of **III**. After completion of the exothermic reaction, excess ethanol was distilled at reduced pressure, and the residue was distilled; yield of **XI** 15.9 g (88%), bp 148–150°C (70 mm Hg),  $D_4^{20} = 2.1105$ ,  $n_D^{20} = 1.5349$  [29].

**Tribromoacetamide XII.** Gaseous ammonia was passed through a solution of 8 g of oxidation products of **III** in 20 ml of absolute toluene until the ammonia uptake ceased. The precipitate was filtered off, washed

with water, and air-dried. Yield of **XII** 5.2 g (78%), mp 119–120°C (from ethanol) [31].

**Oxidation of  $\beta,\beta$ -dibromostyrene IV.** The reactor was charged with 26.2 g of dibromostyrene **IV** and heated to 70°C. At this temperature, oxygen was fed (5 l h<sup>-1</sup>) for 180 h. Distillation of 10 g of the oxidation products gave 7.4 g (74%) of phenylbromoacetic anhydride **XIII**, bp 140–143°C (20 mm Hg),  $D_4^{20} = 1.8557$ ,  $n_D^{20} = 1.6000$  [32].

**Phenylbromoacetic acid XIV.** A mixture of 10 g of oxidation products of **IV** and 10 ml of water was allowed to stand at 20°C for 12 h. Low-boiling products were evaporated in a water-jet-pump vacuum, and the residue was vacuum-distilled. Yield of acid **XIV** 5.9 g (77%), mp 84°C (from ethanol) [23].

**Ethyl phenylbromoacetate XV:** bp 141–143°C (8 mm Hg),  $D_4^{20} = 1.4165$ ,  $n_D^{20} = 1.5415$  [32].

**Phenylbromoacetamide XVI:** mp 146°C (from water) [32].

**Oxidation of  $\alpha,\beta,\beta$ -tribromostyrene V.** Similarly to the oxidation of **IV**, 24 g of **V** was oxidized with oxygen for 250 h. Water (20 ml) was added to 20 g of the oxidation products, and the mixture was allowed to stand at 20°C for 12 h. After evaporation of water and recrystallization of the residue from petroleum ether, 10.9 g (72%) of phenyldibromoacetic acid **XVII** was obtained; mp 102–104°C (from CCl<sub>4</sub> : petroleum ether = 1 : 1) [23].

## CONCLUSIONS

(1) Liquid-phase oxidation of bromovinyl compounds with oxygen in the range 20–100°C was studied, and conditions for selective preparation of  $\alpha$ -bromoacyl bromides were found. The primary oxidation products are bromooxiranes; their maximal content in the oxidation products reaches 60%. In the course of distillation, hydrolysis, alcoholysis, aminolysis, and acidolysis, bromooxiranes quantitatively transform into the corresponding  $\alpha$ -bromo carboxylic acid derivatives.

(2) Oxidation of some bromovinyl compounds with molecular oxygen yields, along with  $\alpha$ -bromoacyl bromides, also the product of addition of bromine to the double bond. Aromatic substituents at the double bond considerably decrease the rate of oxidation of bromovinyl compounds.

(3) Liquid-phase oxidation of bromovinyl compounds occurs exclusively at the double bonds. The bromooxiranes formed in the process are insufficiently

reactive to induce side reactions (cleavage of the double bond or allyl oxidation).

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